ANGULAR MOMENTUM: 2D AND 3D ROTATION

Chem 2430

Angular Momentum

$$\boldsymbol{L} = \boldsymbol{r} x \boldsymbol{p} = \begin{vmatrix} \boldsymbol{i} & \boldsymbol{j} & \boldsymbol{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$L_x = yp_z - zp_y$$

$$L_y = zp_x - xp_z$$

$$L_z = xp_y - yp_x$$

QM case

$$\hat{L}_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right)$$

Similarly for $\hat{L}_y$ and $\hat{L}_z$

$$\hat{L}^2 = \left|\hat{\boldsymbol{L}}^2\right| = \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{L}} = \hat{L}_x{}^2 + \hat{L}_y{}^2 + \hat{L}_z{}^2$$

$$\hat{L}_y f = \frac{\hbar}{i}\left(z\frac{\partial f}{\partial x} - x\frac{\partial f}{\partial z}\right)$$

$$\left[\hat{L}^2, \hat{L}_x\right] = 0, \left[\hat{L}^2, \hat{L}_y\right] = 0, \left[\hat{L}^2, \hat{L}_z\right] = 0$$

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z, \left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x, \left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y$$

Thus, we cannot know precisely two different components of the angular momentum.

We can know precisely a value of $\hat{L}^2$ and a value of one of it components.

Convention is to specify L_z

Note: the fact that we can specify L^2 does not mean we fully know $\boldsymbol{L}$

What are the eigenvalue equations involving $\hat{L}^2$ and $\hat{L}_z$?

While we could directly address this question, it is useful to first consider a rigid rotor in 2D

$$\frac{-\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\psi = E\psi$$

r is fixed to r_o

If this is a diatomic molecule the appropriate mass is the reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Polar coordinates: $x = r_o \cos\phi,\ \ y = r_o \sin\phi$

Can show that the SE becomes

$$\frac{-\hbar^2}{2\mu r_o^2}\frac{d^2\psi}{d\phi^2} = E\psi$$

https://www.cfm.brown.edu/people/dobrush/am34/Mathematica/ch6

This has the solutions

$$\psi = e^{im\phi} \text{ and } E = \frac{\hbar^2}{2\mu r_o^2} m^2 = \frac{\hbar^2 m^2}{2\text{I}}$$

$I = \mu r_o^2$ = moment of inertia

But what are the allowed values of m?

What are the boundary conditions?

$$\psi(0) = \psi(2\pi)$$

$$1 = e^{i2\pi m}$$

Using the Euler relation, one finds that $m = 0, \pm 1, \pm 2, \ldots,$

$$E = \frac{\hbar^2 m^2}{2I}$$

For a classical rotor $E = \dfrac{|\ell|^2}{2\mu r_o^{\,2}}$ where ℓ is the angular momentum

Note: E can = 0 as there is no confining potential

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

$$L_z \psi_m = m\hbar \psi_m$$

So the eigenfunctions of the 2D rotor are also eigenfunctions of $\hat{H}$

This is because $\left[\hat{L}_z, \hat{H}\right] = 0$

Now on to the 3-D case

Spherical coordinates

$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$
$$r^2 = x^2 + y^2 + z^2$$

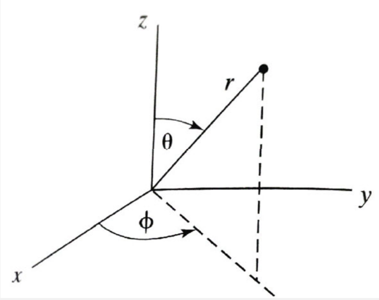

Fig. 5.5 from Levine

$$0 \le r \le \infty$$
$$0 \le \theta \le \pi$$
$$0 \le \phi \le 2\pi$$
$$d\tau = r^2 \sin\theta dr d\theta d\phi$$

$$\hat{L}_x = -i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$
$$\hat{L}_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$
$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

Spherical harmonics $Y(\theta,\phi)$
are common eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$

$$\hat{L}_z Y = bY$$

$$\hat{L}^2 Y = cY$$

Separation of variables

$$Y(\theta,\phi) = S(\theta)T(\phi)$$

$$-i\hbar\frac{\partial}{\partial\phi}(S,T) = -Si\hbar\frac{\partial T}{\partial\phi} = bST$$

or $-i\hbar\dfrac{dT}{T} = bd\phi$

$$T = Ae^{ib\phi/\hbar}$$

$$\Rightarrow b = m\hbar,\ m = 0, \pm 1, \pm 2, \ldots,$$

$$T(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi}$$

$$\hat{L}^2 Y = cY$$

$$\hat{L}^2 ST = cST$$

$$-\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)ST = cST$$

$$-\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}(-m^2)\right)ST = cST$$

$$-\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{-m^2}{\sin^2\theta}\right)S = cS$$

In treating this one usually introduces a change of variables

$$\omega = \cos\theta, -1 \le \omega \le 1$$

$$\left(1-\omega^2\right)\frac{d^2G}{d\omega^2} - 2\omega\frac{dG}{d\omega} + \left[\frac{c}{\hbar^2} - \frac{m^2}{1-\omega^2}\right]G = 0$$

The first few solutions can be found by inspection. The general solution can be found using the series solution approach

$$c = \ell(\ell+1)\hbar^2, \ell = 0,1,2,3$$

$$|\underline{L}| = \sqrt{\ell(\ell+1)}\hbar$$

For a given value of $\ell, m = -\ell, -\ell+1, \ldots 0, \ldots, \ell$

$$Y_\ell^m(\theta,\phi) = \frac{1}{\sqrt{2\pi}} S_{\ell,m}(\theta) e^{im\phi}$$

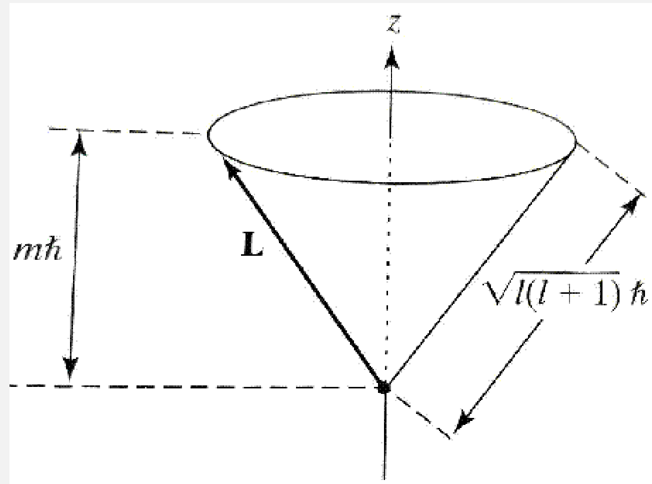

Fig. 5.6 from Levine

$$S_{0,0} = \sqrt{2} / 2 \quad \text{~s}$$

$$S_{1,0} = (\sqrt{6} / 2)\cos\theta$$

$$S_{1,\pm1} = (\sqrt{3} / 2)\sin\theta$$

~p

$$S_{2,0} = (\sqrt{10} / 4)(3\cos^2 - 1)$$

$$S_{2,\pm1} = (\sqrt{15} / 2)\sin\theta\cos\theta$$

$$S_{2,\pm2} = (\sqrt{15} / 4)\sin^2\theta$$

d

Y_1^0 Nodes due to θ

$Y_1^{\pm1}$ Nodes due to ϕ

Y_2^0 Nodes due to θ

$Y_2^{\pm1}$ one θ, one ϕ node

$Y_2^{\pm2}$ Nodes due to ϕ

**Note how *m* quant # is "passed" to the θ Eq. Impacts degeneracy but not the energy.

3D rigid rotor

$$\hat{H} = \frac{\hat{L}^2}{2\mu r^2}\psi = E\psi$$

So $E = \frac{\hbar^2}{2I}\ell(\ell+1)$ and for each ℓ there is a $2m+1$ degeneracy (different m_l values)

A natural extension would be to consider a particle in a spherical box of radius $r = r_o$, with zero potential inside the box and infinite potential outside.

Separation of variables in spherical coordinates.

$$\psi = R(r)\Theta(\theta)\Phi(\phi)$$

R Eq quantizes the energy.